ESR IN WIDE FREQUENCY RANGE FROM 5 TO 24000 MHz
IN PRISTINE TRANS-POLYACETYLENE

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We demonstrate usefulness of frequency dependence study of Electron spin resonance down to several MHz to investigate a frequency spectrum of electron spin dynamics in the low dimensional systems.

Trans-polyacetylene is well known as a prototype of simplest conjugated polymer conductor which conductivity reached as high as $10^5$ S/cm by doping with Iodine [1]. A charged carrier of this system is considered to be charged topological solitons, because a ground state of t-polyacetylene is doubly degenerate. In pristine t-polyacetylene the topological neutral soliton is present as shown in Fig.1 and gives a sharp ESR signal which intensity is about 1 spin per 2000-3000 Carbons.

In this communication we have studied the frequency dependence of ESR $T_1$ and $T_2$ (line width) to investigate the neutral soliton dynamics in t-(CH)x and t-(CD)x. When the electron spins diffuse more faster than a frequency of hyperfine coupling constant, i.e. extreme narrowing case, the relaxation rates reflect the frequency spectrum of the spin motion. The pristine polyacetylene is a good one-dimensional system with an anisotropy ratio larger than $10^5$. Analysis of anisotropic random walk model gives a dimensional cross-over of the frequency spectrum of the spin motion from 1-D limit proportional to $\omega^{-1/2}$ to 3-D limit of frequency independent behavior, through 2-D regime of log-$\omega$ [2].

ESR $T_1$ [3] showed the dimensional cross-over from 1-D to 3-D without 2-D regime, which is consistent to the crystal structure of polyacetylene and NMR analysis [4]. ESR $T_2$ (linewidth) was completely consistent with $T_1$ and was found an interesting broadening at low frequencies in t-(CH)x, which was not found in t-(CD)x [5]. This anomalous broadening can be ascribed to a static non-secular broadening under the condition that the dipolar (anisotropic) hyperfine coupling constant $d$ with the proton nucleus becomes greater than the resonance frequency $f$. In this condition the electron spin sees full proton moment, but not reduced one by the Larmor precession. It is known that the neutral soliton is delocalized over about 15 Carbon atoms, which means that the maximum spin density on the Carbon atom should be smaller than unity. The frequency where broadening starts corresponds to the anisotropic hyperfine constant $d$ multiplied by the maximum spin density on the Carbon atom. With the estimated anisotropic hyperfine constant $d$, we can estimate the maximum spin density as $\rho=0.14-0.18$, which agrees well with that obtained by ENDOR technique [6].